

SWRCB- Agreement #00-200-180-01 Quarterly Report of July 10, 2003

Sources of Selenium, Arsenic and Nutrients in the Newport Bay Watershed

This report will be structured according to the tasks in the original scope of work.

Task 1: Project Management and Administration

Task 1.1 Project administration is proceeding apace.

Task 1.2 The fourth quarterly report is the document you are reading. We have also been engaged in several meetings and phone conversations with board representatives detailing our project progress.

Task 1.3 We have not yet received the one-page summary form from the board.

Task 1.4 Subcontract documents have been delivered to the board.

Task 1.5 This task is not yet applicable.

Task 2: Quality Assurance Plan

Task 2.1 The quality assurance plan has been delivered to the board's designated representative for her review.

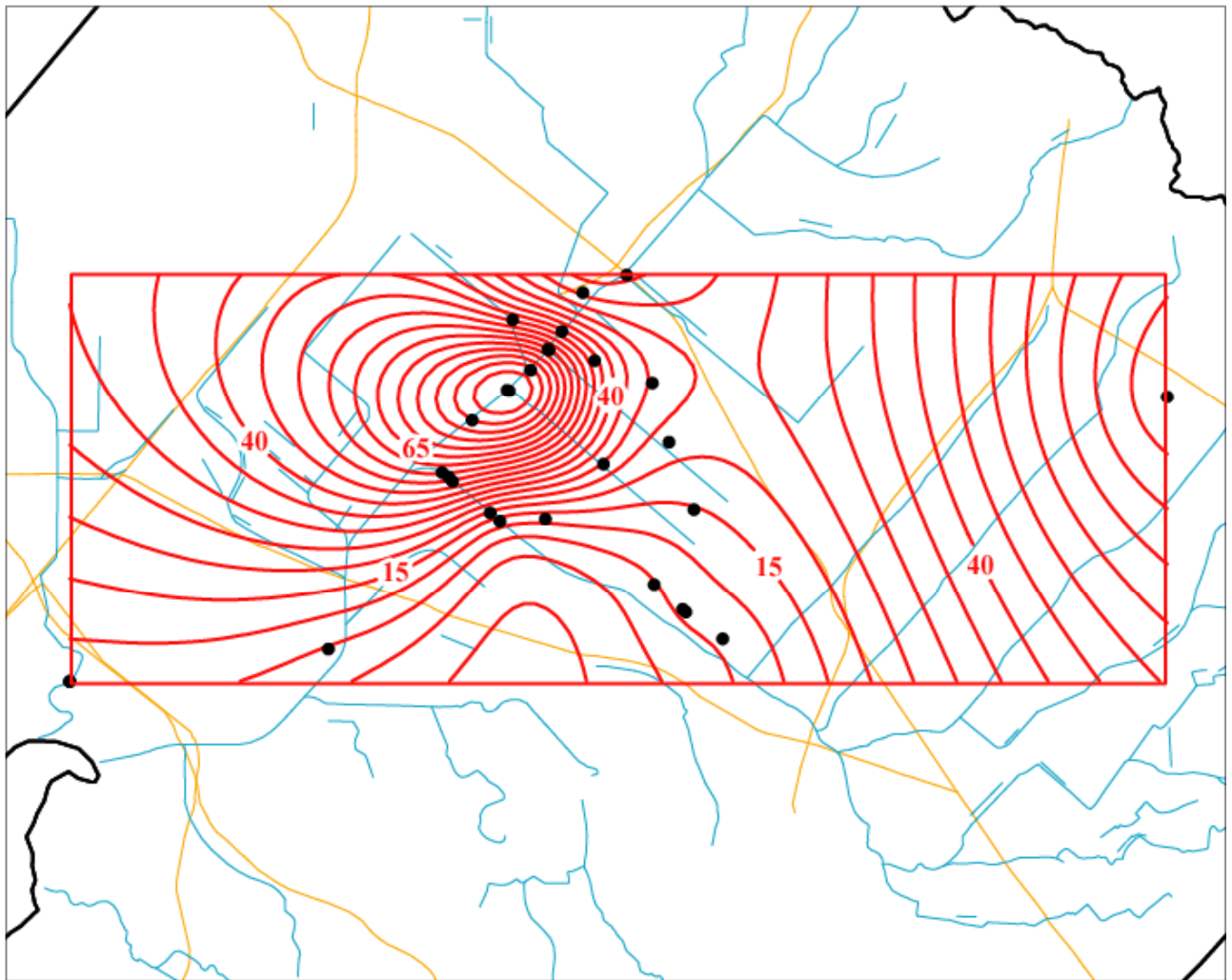
Task 3: Monitoring Program

Task 3.1 Atmospheric Deposition

Atmospheric deposition sampling has continued at our wet and dry bucket collector at the San Joaquin marsh. Total dry deposition has been monitored on a bi-weekly basis throughout the past quarter. When it rains we have also collected wet deposition. When it rains we collect both the wet and dry buckets each week. Dry deposition has varied from a low rate of $0.74 \text{ kg-N ha}^{-1} \text{ year}^{-1}$ up to a high rate of $28 \text{ kg-N ha}^{-1} \text{ year}^{-1}$ (inorganic nitrogen). The mean rate of dry deposition for the six months of sampling so far is $9.3 \text{ kg-N ha}^{-1} \text{ year}^{-1}$. At this mean rate loading to the surface of Newport Bay would be approximately 6200 pounds per year. Using the highest rate observed the rate would be about 19000 pounds per year and the low rate of dry deposition results in a rate of 497 pounds per year. These calculations are based on an open surface water area of the bay of 752 acres. In light of the 2007 TMDL for total nitrogen for the bay of 154,000 pounds per summer season and around 300,000 pounds per year when winter TMDL's are instated in 2012 the atmospheric dry deposition rates above are small but significant contributors of loading to the bay. The 14 wet deposition collections to date indicate that very small loadings of N to the bay directly from rain. Total deposition for the three rain events samples is about 0.56 kg ha^{-1} . This rate of deposition is far below any uncertainty level we may have about loading to the bay.

Task 3.2 Groundwater Contaminant Delineation

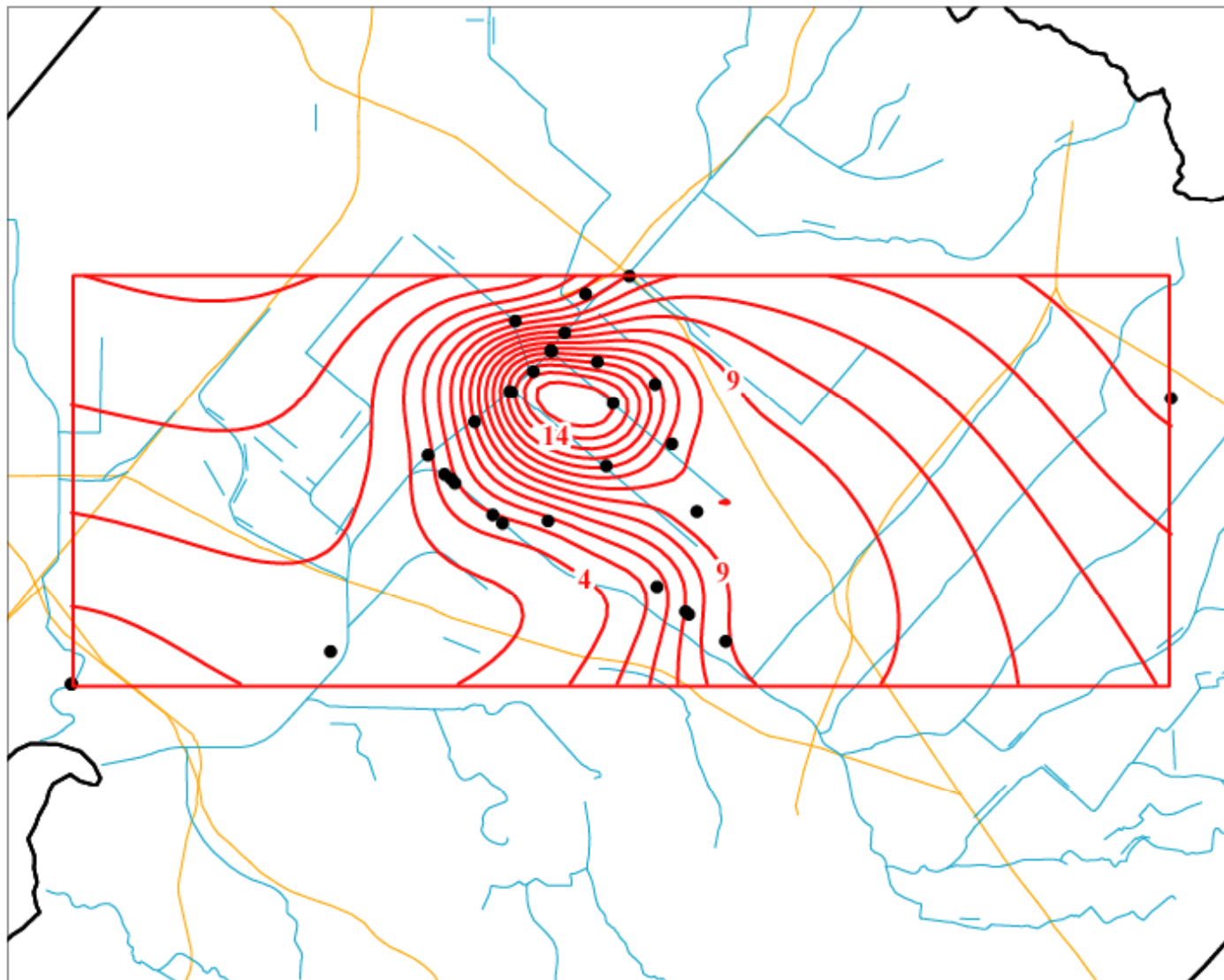
Monitoring of springs and weepholes in the San Diego Creek drainage continues. Enough data has been collected to map groundwater concentrations of Se, As and nitrate in the central part of the Tustin plain (Figures 3.2.1, 3.2.2 and 3.2.3). These figures indicate the growing scope of the area of concern as we move from arsenic to selenium to nitrate as the constituent of interest. In all cases the highest concentrations of all three constituents occur in and around the confluence of Peters Canyon wash and Como channel. The high selenium in the far east of the Se diagram is Tomato Spring. This data indicates that this area may be **the original source region of Se** to the historic Swamp of the Frogs. Within the historic swamp for As and Se the origin appears to be geologic and of a fairly narrow geographic extent. Of particular note is the narrower area with high As concentrations (directly next to Peter's Canyon wash) and the fact that the highest NO_3^- concentrations are farther downstream indicating that longer and deeper flow paths are responsible for the highest NO_3^- concentrations in groundwater. While not easily evident on the contour maps nitrate concentrations actually decline in the hotspot. These maps now reflect only our most recent data and are fairly stable. They are now good enough to aid in decision making regarding Se, As and NO_3^- contamination of groundwater.



Selenium Concentration (ug/L)
Figure 3.2.1



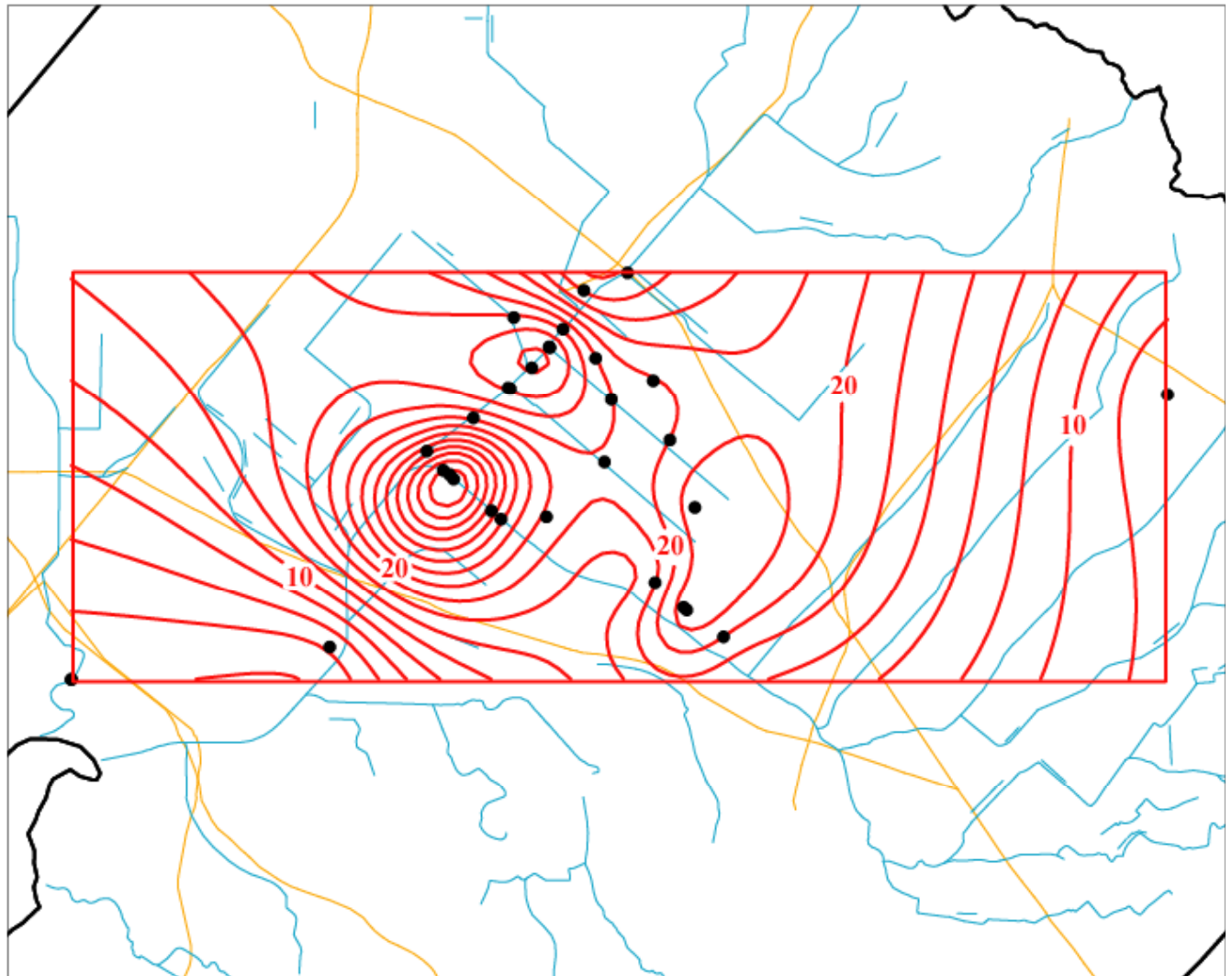
Figure 3.2.1 Spatial extent of Selenium in the Subsurface of San Diego Creek, concentrations are highest in the historic Swamp of the Frogs and particularly on the boundary of the historic marsh. Note high concentration at far right, this is Tomato Spring this may represent the original source region of the Se found in the Swamp of the frogs.



Arsenic Concentration (ug/L)
Figure 3.2.2



Figure 3.2.2 – Spatial Extent of Arsenic in the Subsurface of the San Diego Creek Watershed. Similar to Se As concentrations are highest in the area of the historic swamp of the frogs. However the As hot spot seems to be more centrally located in the swamp of the frogs while the high Se concentrations are more widespread..



Nitrate Concentration (mg/L)

Figure 3.2.3



Figure 3.2.3 Spatial Extent of Nitrate-N in subsurface of San Diego Creek. High nitrate concentrations are prevalent in most of the samples of shallow groundwater in the San Diego Creek basin. The highest concentrations are the farthest downstream locations particularly near the confluence of San Diego Creek and Peter's Canyon Wash. Concentrations of nitrate actually decline in the hotspot area.

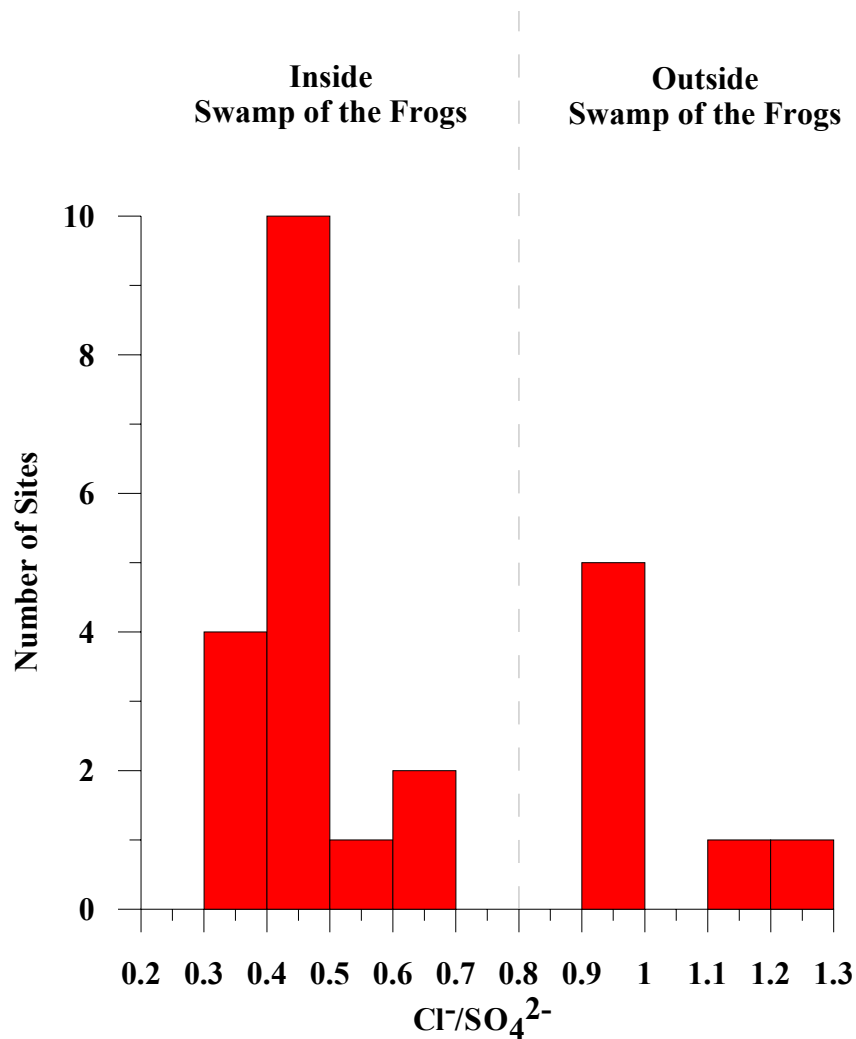


Figure 3.2.4 The $\text{Cl}^-/\text{SO}_4^{2-}$ ratio of groundwater samples can be used to delineate the boundary of the historic Swamp of the Frogs under several assumptions. 1. Chloride is a conservative hydrologic tracer. 2. Sulfate is not conservative and an increase from oxidative dissolution of metal sulfide minerals would show an associated decrease in the ratio.

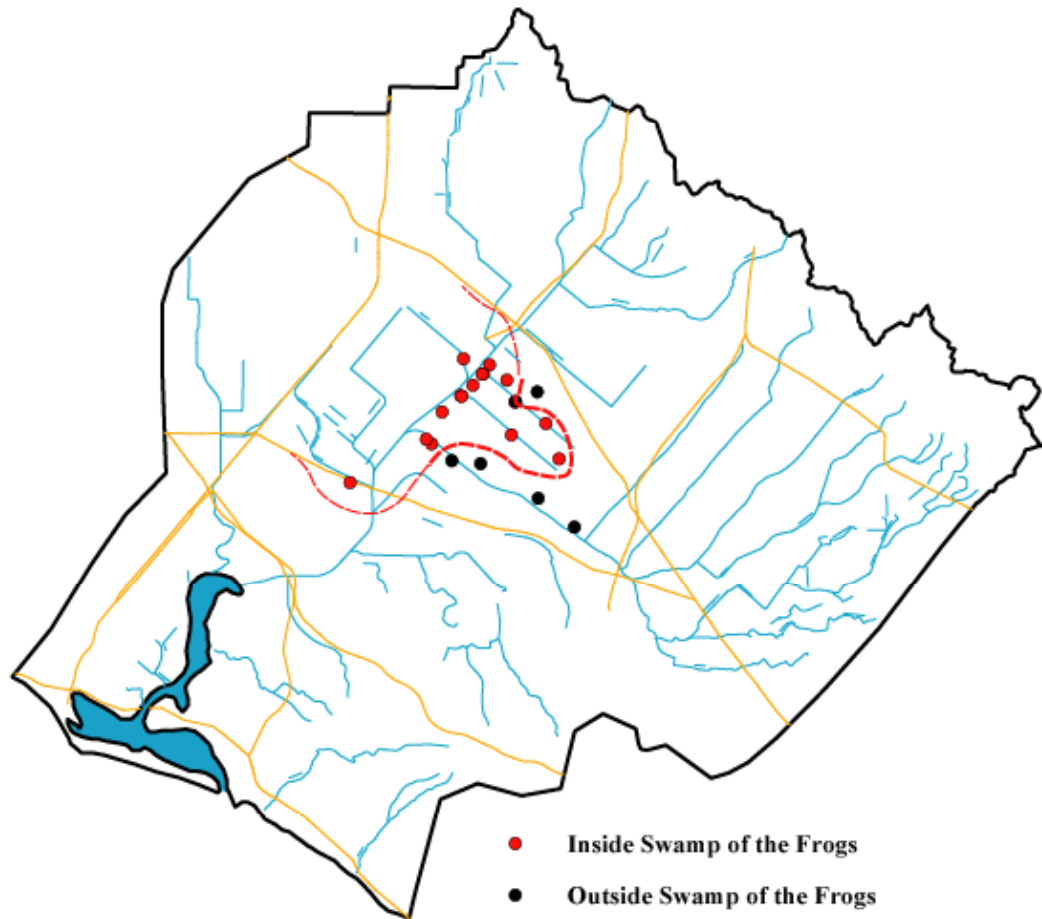


Figure 3.2.5 The CI/SO₄ delineation is presented here in map form. Several other watershed locations have been sampled, but data is not yet available to make a determination. The thicker red line indicates a relative amount of confidence for the Swamp of the Frogs boundary.

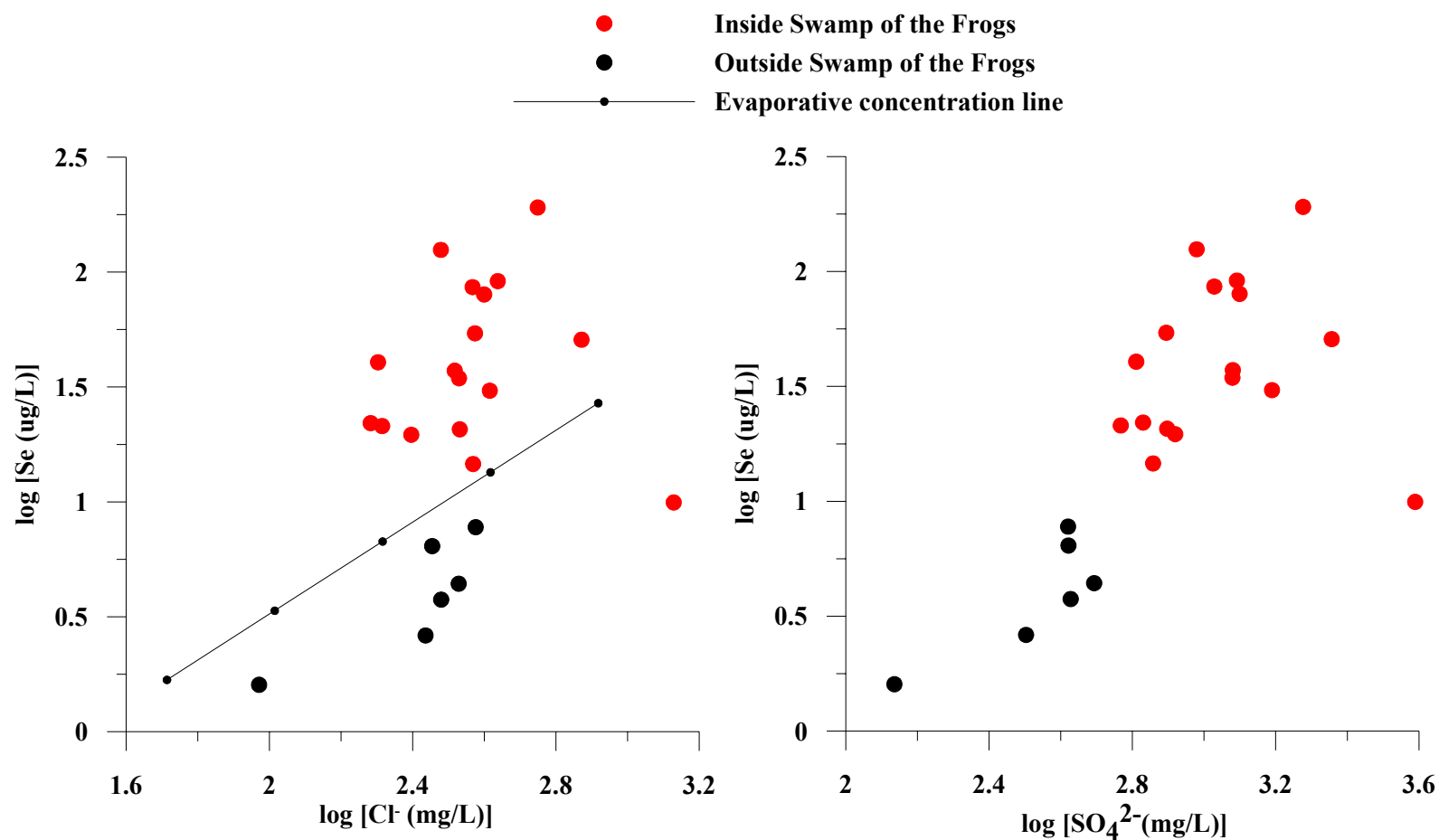


Figure 3.2.6 Cl^- and SO_4^{2-} concentrations were used to delineate the boundary of the Swamp of the Frogs. These can also be used with Se concentrations to understand groundwater sources. The plot on the left shows the evaporative concentration line for local recharge waters. This shows that the groundwaters within the historic swamp have been enriched with Se through dissolution and desorption. The plot on the right infers co-located oxidation of Se and S minerals, with groundwaters receiving significant amounts of each.

Task 3.3 Groundwater Flux and Source

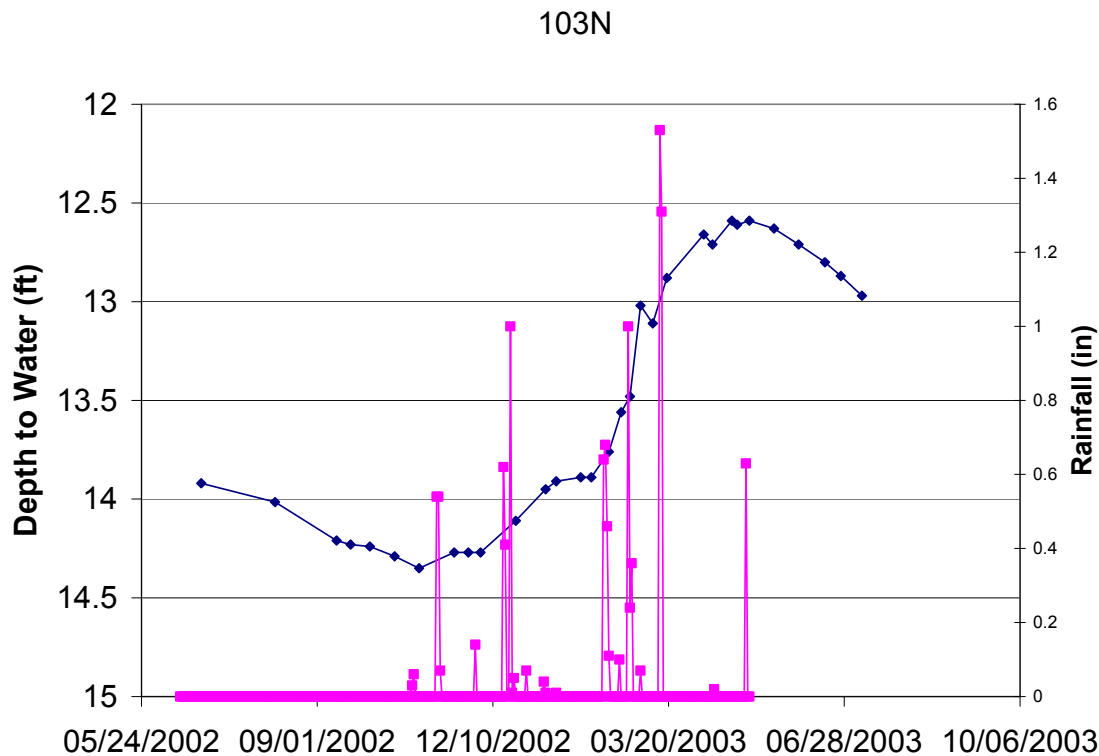


Figure 3.3.1 - Water Level Measurements: Water level measurements have been collected at two-week intervals from IRWD wells. In response to rainfall, there has been an observed increase in groundwater levels in the shallow aquifer. The increase in groundwater varies between .25-.09 ft. Water levels will continue to be monitored twice monthly. This rapid rise after rainfall indicates the likely source of water to the shallow aquifer is from pluvial recharge rather than from irrigation related recharge or from mountain front processes.

Hydrographs

Shallow groundwater wells continued to be measured since the previous quarterly report. There has been a marked decrease in the amount of precipitation since the previous report. As precipitation is the primary source of recharge to the shallow aquifer, the decrease in precipitation is reflected in the depth to the water table. The graph of well 103N (Figure 3.3.1) displays this relationship clearly. The decrease in groundwater level has been recorded in varying degrees within the other wells.

Time Series Hydrographs

Water levels measured in shallow water wells since Summer, 2002 indicate variable response to seasonal change (Figure 3.3.1). Water wells closest to Peters Canyon Wash show the least response to seasonal change, possibly because the major channels tend to stabilize water levels in the shallow aquifer. Several wells showed increasing water levels after September 2002 in response to greater precipitation rates and lower evapotranspiration. Downward moving wetting fronts are apparently reaching the water table within a few days to a few weeks after precipitation events.

Water levels will continue to be monitored during the rainy season. Water samples will be collected simultaneously from groundwater and streams to determine if there is a correlation between nutrient and trace element loads in groundwater and fluctuating water levels in the aquifer.

Groundwater Source

A figure showing the water isotope data for San Diego Creek Watershed is available in a separate file (see attached). This isotopic data indicates that the water in the San Diego Creek watershed is of generally local origin with the O-18 and D isotopic signature being that of mean rainfall in the basin. The samples with highly negative D or O-18 signatures may indicate some mixing with imported water (most likely Santa Ana River water).

Sulfur Isotopes

During the recent reporting period, several groundwater samples were collected for sulfur isotope analysis. Analysis of sulfur isotopes was performed in the Isotope Geochemistry Laboratory in the Department of Geological Sciences, University of Arizona. Samples were collected from springs and weepholes at several locations within and outside of the region formerly occupied by the historic Swamp of the Frogs marsh (Figure 3.3.2).

East of Peters Canyon Wash, measured $^{34}\text{S}[\text{SO}_4^{2-}]$ were slightly positive in all but one sample. West of Peters Canyon Wash, groundwater isotope values were negative in all samples (Figure 3.3.2). Positive sulfur isotope values varied only slightly, from 1.4 to 2.5 per mil $^{34}\text{S}[\text{SO}_4^{2-}]$. Negative values varied more widely, from -1.9 to -13.5 per mil $^{34}\text{S}[\text{SO}_4^{2-}]$. Positive $^{34}\text{S}[\text{SO}_4^{2-}]$ values may indicate multiple sulfate sources and mixtures, including fertilizers, organic matter, marine salts, and atmospheric deposition (Krouse and Grinenko, 1991). Negative sulfur isotope values are consistent with oxidation of Fe-sulfides and dissolution of second-cycle terrestrial evaporitic salts that may have been derived originally from oxidation of metal sulfides (e.g., Thernardite or Mirabolite salts).

Negative values of $^{34}\text{S}[\text{SO}_4^{2-}]$ coincide with the Swamp of the Frogs marsh region and with the region identified by Trimble (1998) as an “ephemeral lake” that created alkali salt deposits. This “lake” which is mapped at the southern edge of the Swamp of the Frogs marsh, existed before the historic period of agricultural development in the study area (circa 1850). This lake region, now drained by Lane Channel, might also have formed from evaporative discharge (wicking) of shallow groundwater at the western boundary of the Swamp of the Frogs marsh, and not strictly by evaporation of surface water in an ephemeral lake.

Two spring samples on the east side of Peters Canyon Wash have positive $^{34}\text{S}[\text{SO}_4^{2-}]$ values (1.4 and 1.8 per mil). These springs have consistently produced some of the highest selenium, sulfate, and arsenic concentrations in the study area ($> 100 \text{ ug/L Se}$; $> 1500 \text{ mg/L SO}_4$, $> 25 \text{ ug/L As}$). These springs are mapped near the margins of the historic Swamp of the Frogs marsh

(Trimble, 1998; Hibbs and Lee, 2000). The hydrochemical signature of these springs is interpreted to be indicative of oxidation of Fe-sulfides that precipitated in the historic marsh. Even so, the positive sulfur isotope signature tested in these springs is generally at-odds with the concept of oxidation of Fe-sulfides.

The anomaly observed at the springs will be investigated further. First, the springs will be retested for sulfur isotope signatures. An expanded suite of S-isotopes will also be collected from shallow water wells, surface waters, and other springs and weepholes throughout the study area. Oxygen isotopes will also be tested in the sulfate residuals in groundwaters. The combination of sulfur and oxygen isotopes tested in sulfate extracts will allow us to further discriminate between origins of sulfate in the region.

The positive correlation between sulfate, selenium, and arsenic in parts of the Swamp of the Frogs marsh region underscores the necessity of deciphering the origins of sulfate in local groundwaters. It must be kept in mind that the bulk sulfate isotope signature of any groundwater represents possible mixtures of multiple sources of sulfate (and sulfur) in the study area. Sulfate has already been shown to be derived in part by insitu oxidation of metal sulfides. Other sources of sulfate in shallow groundwater are derived from a variety of endmember sources, including atmospheric precipitation falling directly onto the Tustin Plain; urban runoff derived from potable water and reclaimed wastewaters, irrigation by local groundwaters; irrigation by State Project water; and runoff from the Santa Ana Mountains and San Joaquin Hills (along with some dissolution and/or oxidation of sulfur in headwater catchments). Future efforts will focus on identifying the isotope and geochemical signatures of these endmember waters.

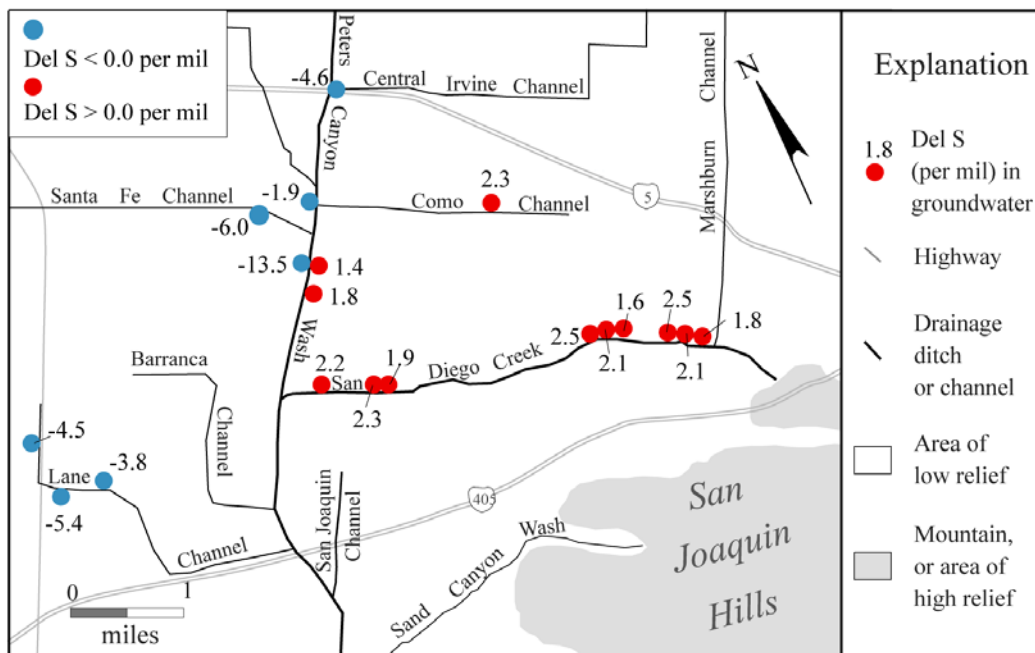


Figure 3.3.2. Per mil values of sulfur isotopes in groundwaters collected from springs and weepholes in the study area. Lane Channel Studies.

Lane Channel Studies

Surface water studies by OCPFRD and Hibbs and Lee (2000) showed that Lane Channel consistently contained moderately high concentrations of nitrogen, selenium, and salinity (>8 mg/L total N; > 14 ug/L Se; and > 5000 uS conductivity). Data collected since 2002 by the research team has shown the same general results. More recent data also indicates that arsenic concentrations are low and sulfate concentrations are very high in Lane Channel (< 3.0 ug/L As; and > 1500 mg/L SO₄). In other channels, elevated selenium and sulfate concentrations are frequently correlated to high arsenic concentrations; but not in Lane Channel

Nitrate and selenium concentrations in the current and historical data suggest a demonstrable source of groundwater baseflow into Lane Channel. Accordingly, the research team spent several days in the field during the reporting period performing field evaluations of Lane Channel. The evaluations included gaging streamflows, measuring concentrations of hydrochemical parameters at surface water stations and lateral inflows, and mapping and sampling groundwater discharge outlets, such as weepholes and springs.

Partial analytical results are available at this time. A subset of our findings is presented in Figure 3.3.3. These data indicate that surface flows at upstream stations, midpoint stations, and downstream stations had consistently high concentrations of nitrogen and selenium during field-testing (> 19 ug/L Se; > 9 mg/L total N). Arsenic, on the other hand, was below 4 ug/L at all surface water monitoring stations. Conductivity increased along a downstream trend, from 2260 uS to 5300 uS.

These data suggest substantial groundwater input into Lane Channel that contains high conductivity, high selenium, high nitrogen, and low arsenic. This was confirmed by sampling local groundwater. Field studies indicated the existence of several groundwater weepholes and springs below the 55 freeway (Figure 3.3.3). Groundwater in these springs and weepholes usually exceeded 25 ug/L Se and 15 mg/L total N. Conductivity in groundwater was also very high, and arsenic was less than 4 ug/L (Figure 2).

High sulfate and selenium concentrations and low arsenic concentrations in groundwater near Lane Channel are not consistent with earlier findings. Earlier findings indicated that high selenium and sulfur concentrations, from oxidation of metal sulfides that formed in the Swamp of the Frogs marsh, were often correlated to high arsenic concentrations. Differences in land regions prior to development may provide insights on these important differences.

As mentioned in the section on sulfur isotopes, Lane Channel drains a region historically identified by Trimble (1998) as an ephemeral lake, identified by historical 1901 soil survey maps as containing concentrated alkali salt deposits. While the evaporation of ephemeral floodwaters could create these alkali salt deposits, it is perhaps even more likely that the evaporitic salt crusts originated from evaporation of shallow groundwater at the southern edge of the Swamp of the Frogs marsh. Such salt crusts are best developed in areas where the water table is within 1 meter of the surface. Areas of evaporitic salt crusts are characterized by poor development of vegetation, which would tend to preclude the existence of sufficient organic matter needed to produce a highly reducing environment.

Mineralogical assemblages associated with terrestrial evaporitic salt crusts often contain sulfate-bearing minerals such as Mirabilite and Thenardite. We have already confirmed the existence of extensive Thenardite salts precipitating along the sides of Lane Channel. These types of efflorescent sulfate minerals may contain elevated concentrations of selenium, their open lattice

structures incorporating the selenate anion in the sulfate space. The possible and continual leaching of these residual alkali salts from within the vadose zone near Lane Channel is a possible explanation for high sulfate, high selenium, and low arsenic concentrations. Negative sulfate isotope signatures are also consistent with the signature expected in this specific region for dissolution of terrestrial evaporites. Accordingly, a new hypothesis to be investigated is the existence of an alkali salt region south of the Swamp of the Frogs marsh region that was the evaporative discharge area for waters (surface waters and groundwaters) that moved into and through the historic Swamp of the Frogs marsh region. Evaporation of these waters could produce salts containing high sulfate, high selenium, and low arsenic in soil profiles near present-day Lane Channel. Leaching of selenium-bearing, efflorescent sulfate salts through vadose zone profiles could then account for the anomalous geochemical signatures of surface water and groundwater near Lane Channel.

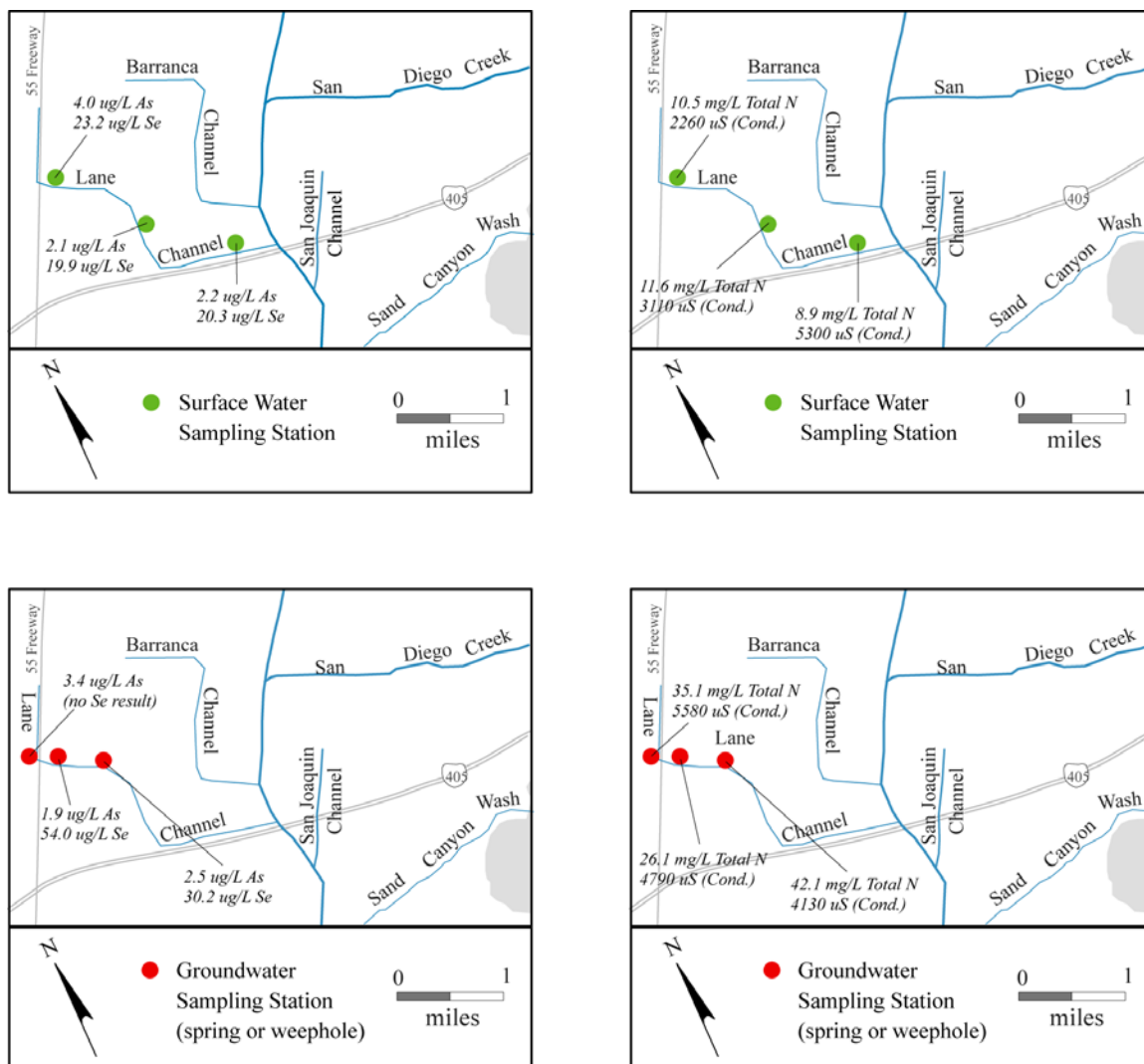


Figure 3.3.3. Selected results of sampling of Lane Channel and nearby groundwaters for hydrochemical parameters.

Task 3.4 *Baseflow Analysis*

We conducted a stream baseflow study at the end of June on the same reach of Peters's Canyon as before. However the data is not yet ready to report these results. We have continued to do some peepers studies and one along San Diego Creek bore fruit and we found a gaining reach of the stream with higher nitrate at depth than in the stream.

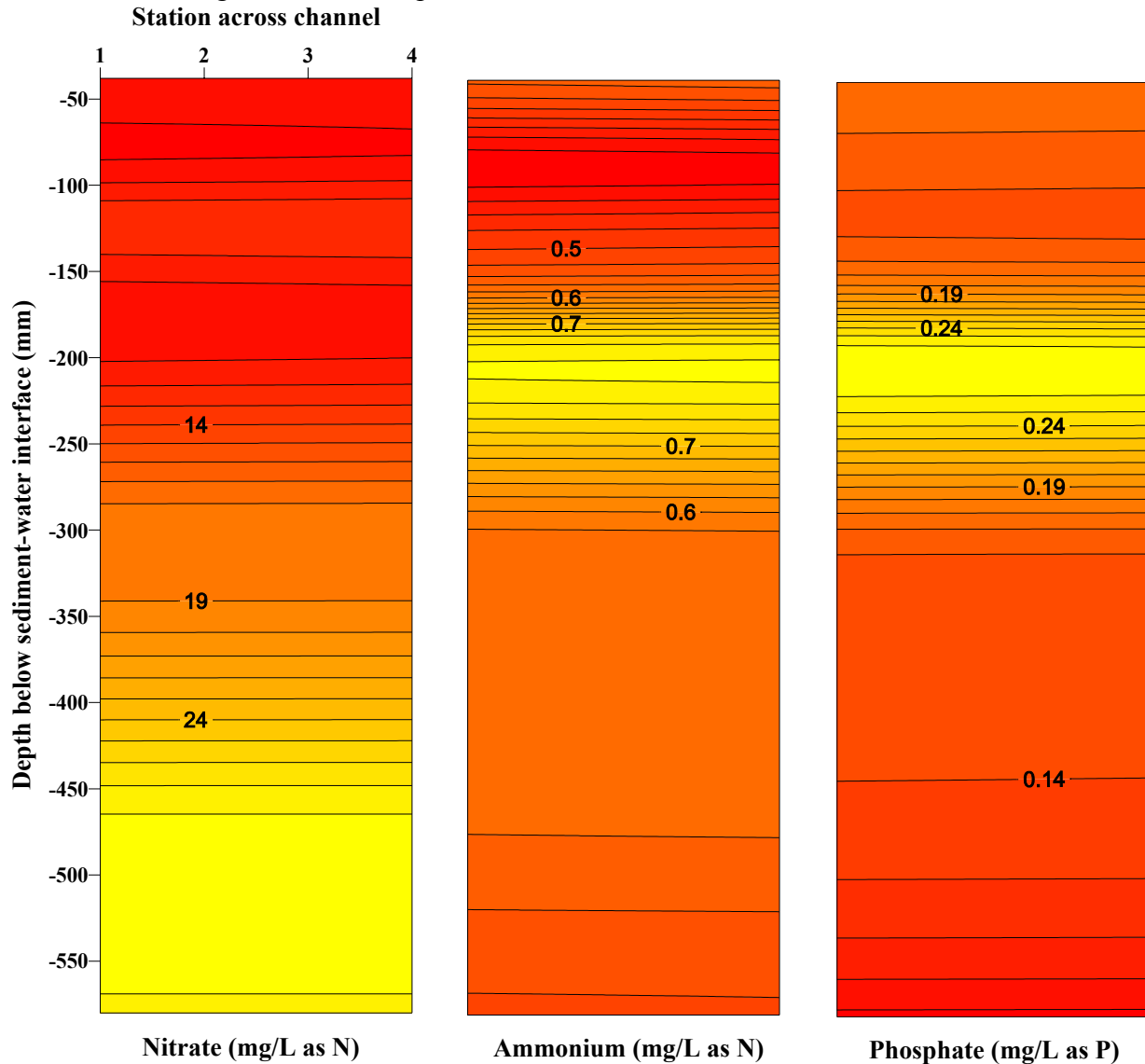


Figure 3.4.1

Peepers study conducted on Upper San Diego Creek above Jeffrey Road. Nutrient results indicate gaining conditions in this reach of the channel. Nitrate concentrations are highest with depth and reach nearly as high as local groundwaters. This indicates some reduction is present in the sediment. Also supporting localized reduction are maximums of ammonium and phosphate at approximately 2 cm below the sediment-water interface. However, because ammonium and phosphate do not increase with depth, these also indicate the presence of upwelling groundwaters.

Task 3.5 Dewatering Operations

The Denitrification Plant operated by Cal Trans was designed in response to the dewatering of high nitrate groundwater from the underpass of Highway 261. The plant has been temporarily shutdown. Monitoring of the Culver underpass sump continues.

Task 3.6 – Detention Basins

Several detention basins were sampled in May. Analysis is ongoing for Se and As content and results should be in soon. The detention basins in Hicks and Round Canyon were sampled.

We have also conducted Se concentration and speciation analysis on sediment samples from the OCPFRD detention basins near the IRWD Michelson plant.

Table 3.6.1 Selenium speciation in sediment samples collected November 2002, prior to winter rains

	Total Se	Se (IV)	Se (VI)	Organic Se	Elemental Se	OM* - Se	Residue Se	% Immobile	% Se (IV)	% Se (VI)
SDC @ Campus	2.195	0.766	0.182	0.255	0.375	0.613	0.004	56.811	34.897	8.292
SDC @ Marsh Inlet	2.078	0.477	0.095	0.539	0.620	0.311	0.035	72.425	22.955	4.572
PCW below CC	1.162	0.333	0.014	0.236	0.183	0.389	0.007	70.138	28.657	1.205
Bank - PCW below CC	0.461	0.089	0.051	0.077	0.000	0.227	0.018	69.848	19.306	11.063

The channel bottom and retention basin sediments appear to be sinks for selenium. 56.8 to 72.4% of Se is found in reduced, immobile forms while an addition 19.3 to 34.9% is found as slightly reduced, less mobile Se (IV).

*OM = organic materials related

Task 3.7 Open Space

Sites were selected on Hicks canyon at the Hicks canyon detention basin and in Rattlesnake canyon above the Avocado groves. Flow has only been observed since at the Hicks' Canyon site (Table 3.7.1). Results thus far indicate no cause for concern as regards nutrients from the open space in the catchment. Se and As analysis have now been done. These analyses indicate elevated Se and As concentrations in storm flow in Hicks Canyon. This storm data long with the data at Tomato spring indicate that this area is the original source region of Se and As within the San Diego Creek/Newport Bay watershed.

Table 3.7.1 Storm Flow Water Quality Hicks Canyon

Date	Time	Se (ug/L)	As (ug/L)	NO3-N (mg/L)	NH4-N (mg/L)	PO4-P (mg/L)	TN (mg/L)	TP (mg/L)
3/15/03	21:00	3.13	4.21	0.29	0.09	0.09	2.09	4.90
3/15/03	0:00	3.9	3.94	0.37	0.08	0.18	3.58	7.50
3/16/03	5:00	10.53	5.14	0.93	0.06	0.35	4.09	6.20
3/15/03	15:00	1.22	4.19	0.30	0.09	0.11	1.84	3.60
3/15/03	15:15	5.86	12.53	0.58	0.05	0.15	2.65	7.20

Task 3.8 Low Level Se

We have determined that are laboratories detection limit for Se is 0.4 ug/L and that our reporting limit is approximately 1.4 ug/L. The reporting limit needs to be further verified with ongoing analyses. We therefore have decided not to send samples off to Columbia Analytical for further analysis of low level Se concentrations

Task 3.9 Hg Sampling

Both rounds of Hg sampling and analysis are complete, results are reported below in table 3.91. Results indicate that Hg should not be of concern at this time as the concentrations are all below the level of concern in aquatic systems.

Table 3.9.1 - Hg Concentrations in San Diego Creek Watershed

Date collected	Location	Hg, total (ng/L)
11/12/02	SDC @ Campus	5.0
11/12/02	PCW @ Barranca	2.7
11/12/02	PCW @ Barranca Dup.	3.6
11/12/02	SDC @ Harvard	3.3
11/15/02	Weephole 10N - SFC @ RR	1.8
11/19/02	EMIC @ PCW	2.9
11/19/02	PCW @ EMIC	6.8
11/19/02	CC @ PCW	5.1
11/19/02	Drain - PCW E. side N. of Warner	2.0
01/02/03	CIC @ Northwood Plaza on Trabuco	3.1
01/02/03	BaC @ Alton	4.4
01/02/03	EMIC @ 17th	1.6
04/07/03	SDC @ Campus	3.4
04/07/03	BaC @ Alton	2.8
04/07/03	PCW @ Barranca	3.4
04/07/03	SDC @ Harvard	2.2
04/07/03	Drain PCW E. Side N or Warner	2.3
04/07/03	Weephole 10N SFC @ RR	2.0
04/07/03	EMIC @ 17th	1.7
04/07/03	CC @ PCW	1.5
04/07/03	PCW @ CIC	3.2
04/07/03	CIC @ PCW	4.5

Task 3.10 Hg QA/QC

Duplicate sample analysis for Hg indicates that Columbia Analytical's results are reliable with the Barranca sample and its duplicate coming in at 2.7 and 3.6 mg/L respectively.

Task 3.11 Selenium Speciation

Selenium speciation results for the last quarter are presented below.

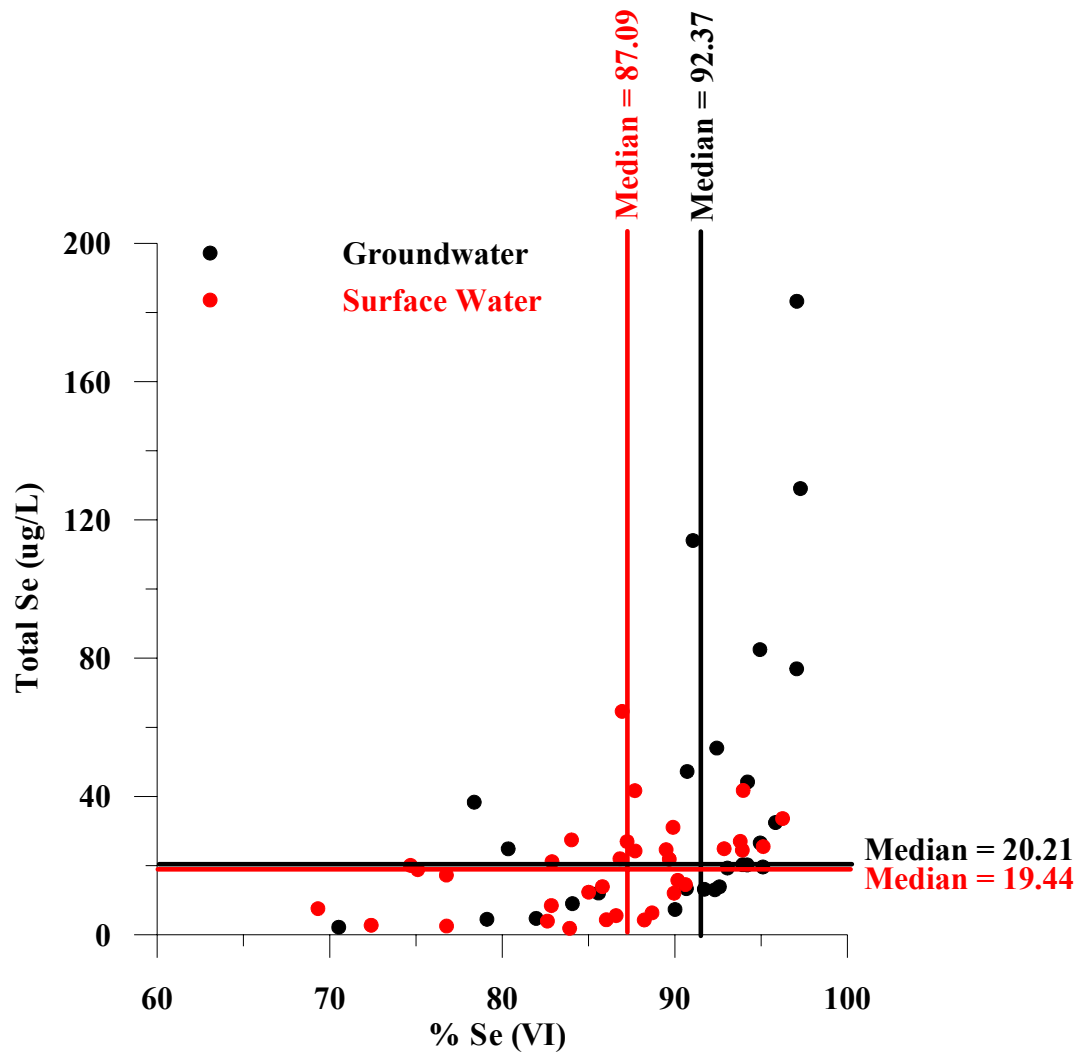
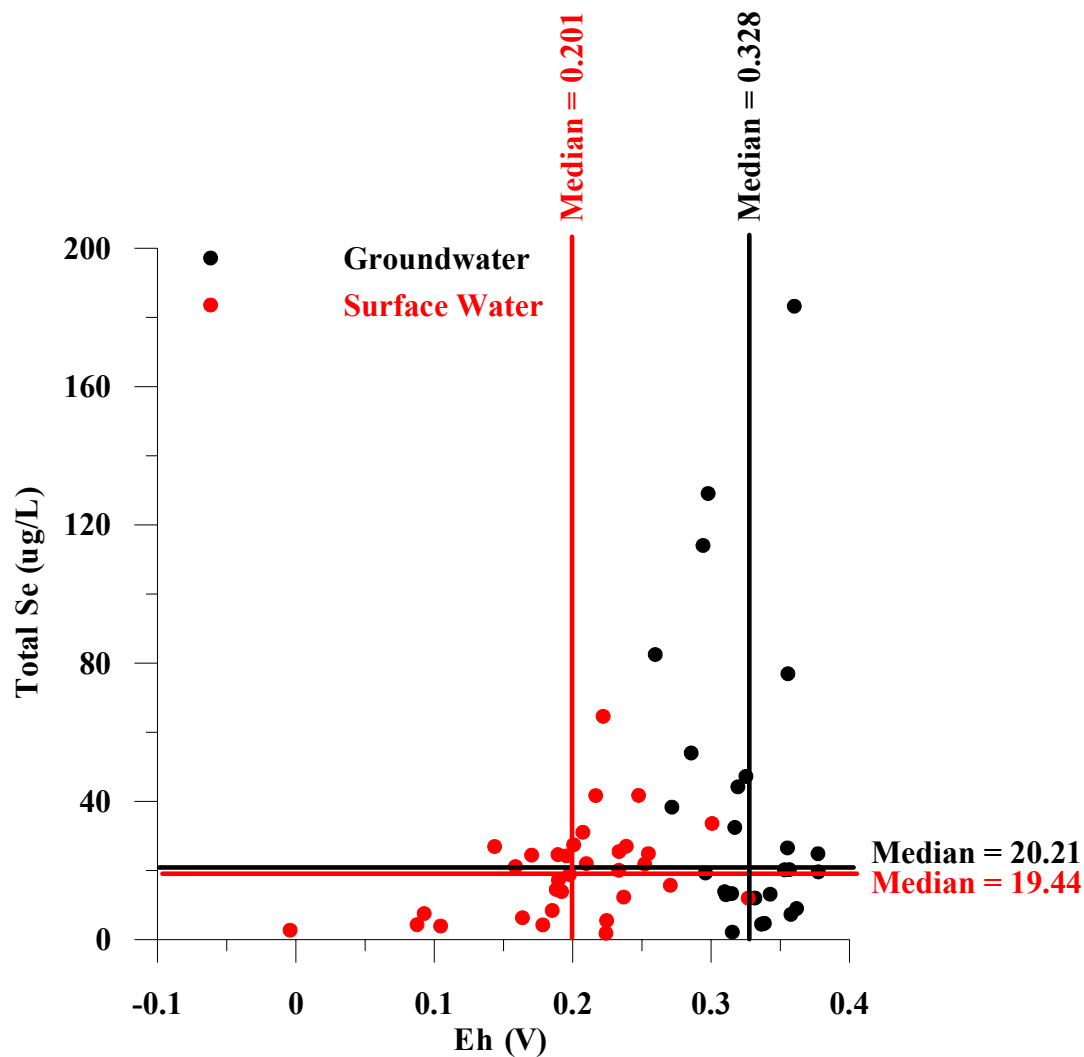


Figure 3.11.1 Groundwaters of the watershed are more oxidizing than the surface waters, as evidenced by a greater median % Se (VI). Though the highest concentrations of Total Se are found in groundwater samples, the median values for both are near 20 ug/L. This is due to lower concentrations in groundwater samples found outside of the historic Swamp of the Frogs as well as surface water drains which have a variable groundwater component.



Task 3.12 QA/QC

Table 3.12.1 – QA/QC Reporting for Project

	Maximum Spike RPD	Maximum Duplicate RPD	Median Spike RPD	Median Duplicate RPD	Spike % Recovery Range	Median % Spike Recovery
Nitrate	3.1	13.3	0.7	3.2	94.9 – 103.1	96.8
Ammonia	5.3	NA	1.8	NA	92.5 – 108.1	94.6
Phosphate	3.3	NA	0.7	NA	84.5 – 101.9	93.0
Total Nitrogen	4.9	55.3	2.2	0.1	90.8 – 107.0	97.7
Total Phosphorus	4.6	NA	1.0	NA	96.4 – 125.4	100.3
Selenium	13.3	1.5	1.2	1.2	80.5 – 106.7	100.1
Arsenic	4.0	NA	1.7	NA	92.0 – 113.8	99.1

The maximum spike Relative Percent Difference (RPD) is the highest spike RPD during the quarter. RPD is a measure of precision, that is, random error.

Duplicates are samples collected at the same time and location. In cases where most duplicate data were less than the quantitation limit duplicate RPD was not reported. In those cases precision may be estimated from spike duplicates.

A spike is a sample to which a known amount of the analyte has been added. Spike recovery is a measure of accuracy. Spiked samples are used to determine the effect of the matrix on a method's recovery efficiency. The range shows the lowest and highest recoveries in the quarter. The median represents typical recovery during the quarter.

The Method Detection Limits (MDL's) for nitrate, ammonia and phosphate were 0.11, 0.06, and 0.03 respectively. The MDL is defined as the minimum concentration that can be measured and reported with 99% confidence that the concentration is greater than zero.

Task 4: Input into TMDL Updating

At this time we can report that our groundwater concentration maps of Se, As, and NO_3^- are stable enough to warrant preliminary decision making in mitigating existing water quality issues in the basin and to avoid future issues related to these contaminants. While, the maps are not final per se the board should feel confident in using this information to aid themselves and others in decision-making. It is also becoming evident from our studies of subsurface conditions in areas where the channel is lined that channel lining with concrete may adversely affect water quality and thus care should be exercised in lining channels with concrete. It should be recognized that lining the channels with concrete decreases sediment export from a channel reach so the benefits of unlined channels need to be weighed against this benefit of lining. We have continued to communicate with various individuals about the implications of groundwater nutrients, Se, and As in the area.

We can confidently say that the source water for the shallow groundwater body in the Tustin plain appears to be mostly locally derived rainfall. This source may include deep groundwater as its isotopic source is similar.

A strong case is being assembled that the source of the Se and As in the groundwater is from sulfide mineral associated Se and As as evidenced by the sulfur isotope and chloride sulfate ratio data. We are continuing to pursue this story to investigate whether high nitrate concentrations in the groundwater may be facilitating the mobility of Se and As out of this groundwater body.

Based on our existing data Mercury is not a concern for water quality conditions in the basin. A final recommendation can be made at the end of the month once all of the data is back from Columbia Analytical.

Task 5: Project Reports

Tasks are not yet applicable.